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AUTHOR(S):

Horiguchi, Kazunori; Kurokawa, Shu; Sakai, Akira

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Conductance and *I-V* characteristics of Au/BPY/Au single molecule junctions

Kazunori Horiguchi,^{a)} Shu Kurokawa, and Akira Sakai

Department of Material Science and Engineering, Kyoto University, Kyoto 606-8501, Japan

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We have investigated the low bias conductance and *I-V* characteristics of single 4,4'-bipyridine (BPY) molecule connected to gold electrodes at room temperature. Exploiting the mechanical controllable break junction technique we statistically determined the most preferred conductance value of Au/BPY/Au single molecule junctions. The measured conductance, $0.01G_0$ (G_0 is the conductance quantum unit), is in good agreement with two of the previous experiments using scanning tunnel microscopy break junctions. The *I-V* characteristics of the Au/BPY/Au junction have been directly measured by varying the bias up to ± 0.5 V while holding the junction at its single molecule state. By comparing the obtained *I-V* curves with those of the Au/1,4-benzenedithiol (BDT)/Au junction, we observed differences in the energy level alignment of BPY and BDT molecules with respect to the Au electrode. © 2009 American Institute of Physics.
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I. INTRODUCTION

Single molecule junctions, in which single molecule is connected to metal electrodes, have been attracting much attention because of their potential applications as active devices in nanoelectronics. For realizing workable molecule devices, it is of crucial importance to understand electronic properties of single molecule junctions because they constitute the key characteristics that are indispensable for designing and controlling the functions of individual single molecule devices. One of such important electronic properties of a single molecule junction is its current-voltage characteristics which provide us not only a junction conductance but also spectroscopic information on the electronic density of states of the junction. Although there have been a number of experiments on single molecule junctions, many of them have been concerned on the junction conductance at some fixed biases, and the entire *I-V* characteristics have been investigated only for few molecule junctions.

In this work, we have measured *I-V* characteristics of a 4,4'-bipyridine (BPY) single molecule bridging across a pair of gold electrodes (hereafter referred to as a Au/BPY/Au junction). The 4,4'-BPY molecule consists of two pyridine rings, with the nitrogen atom of each pyridine ring locating at opposite ends of the molecule. Because a pyridine can bind to metals through the nitrogen-metal bonding, BPY has been utilized as a binder for constructing three dimensional molecular scaffolds.¹ The binding capability of BPY with various metals also makes it a promising candidate, together with thiolates such as benzenedithiol, for an active element or an "alligator clip" for building molecular devices. Recent experiment² shows that the affinity level of pyridine to Au surfaces can be controlled by changing the electrochemical

potential, an observation which implies a possible application of BPY as a switching element. Concerning the molecular conduction of BPY, a number of theoretical and experimental studies have been made for elucidating the carrier transport through metal/BPY/metal junctions.³⁻¹⁹

The first attempt to fabricate single BPY junction was carried out by Xu and Tao.¹⁶ Using scanning tunnel microscopy (STM) junctions consisting of a Au tip and a Au surface, they repeatedly made and broke the Au-Au tip-surface contact in a solution containing BPY molecules while monitoring the conductance. During the contact break, they occasionally observed a series of steps in the conductance trace, which appear below the minimum conductance level of the Au-Au contact. These steplike features can be interpreted as the signature of molecular bridging between the Au tip and the surface. From these featured traces, Xu *et al.* constructed a conductance histogram and found sharp peaks at integer multiples of $0.01G_0$ ($G_0 = 2e^2/h$ is the quantum unit of conductance). They interpreted that the first peak at $0.01G_0$ corresponds to the conductance of single Au/BPY/Au junction, while higher conductance peaks being due to the multiple bridging of BPY. Subsequent two experiments,^{17,18} however, report different results on the single BPY conductance. Hashimoto *et al.*¹⁷ obtained $0.01G_0$ in agreement with the value determined by Xu and Tao.¹⁶ On the other hand, Zhou *et al.*¹⁸ employed the STM junction method similar to those used in Refs. 16 and 17, but found two low conductance values, $4.7 \times 10^{-3}G_0$ and $0.59 \times 10^{-3}G_0$, for the single Au/BPY/Au junction. Theoretical conductance is mainly distributed around $0.005G_0$ – $0.04G_0$,^{3,4,6,8,15} except for some studies in which the calculated conductance is $0.3G_0$ or higher.^{5,10} Recently, Quek *et al.*¹⁹ carried out detailed conductance measurements on Au/BPY/Au and found even lower conductance, which takes two values at $1.6 \times 10^{-4}G_0$ and $6 \times 10^{-4}G_0$. Upon elongating and squeezing the junction, the conductance reversibly switches between these two val-

^{a)}Electronic mail: k.horiguchi@ht7.ecs.kyoto-u.ac.jp.

ues. Based on the conductance calculation on 55 junction geometries, they indicate that the two conductance states correspond to different molecular arrangements; the more squeezed geometry with larger molecular tilting with respect to the junction axis yields higher conductance.

As for the electron transmission through Au/BPY/Au, previous theoretical studies agree that the low-lying peak near the Fermi level in the transmission spectrum is derived from the lowest unoccupied molecular orbital (LUMO) of BPY molecule. However, the position of this peak is different for different calculations, and the theoretical I - V curve shows a large diversity. Some authors^{5,10} found the transmission peak very close to the Fermi level and predicted that the I - V curve steeply increased around the zero bias and tended to saturate at higher biases. On the contrary, other work^{8,9} locates the peak $\sim(0.1\text{--}0.5)$ eV above the Fermi level, and the resulting I - V curve shows wider linear region around the zero bias. In the calculations by Li *et al.*,¹¹ the peak is further away from the Fermi level, and the I - V curve deflects upward around ~ 0.7 V. Also, the junction geometry such as molecular orientation,¹⁹ binding site,^{5,6,8,13} and the Au-Au electrode distance^{7,8,11,12} is known to make a significant influence on the transmission spectrum and sensitively affect the I - V characteristics. For example, Quek *et al.*¹⁹ reported that the LUMO-originated peak, which locates at 1.6–1.8 eV from the Fermi level, shifts with the molecular tilting. This geometrical sensitivity of the theoretical transmission spectrum, together with differences in the calculation scheme, makes the results of theoretical studies quite varied and controversial.

In experiment, Xu and Tao¹⁶ obtained the conductance histogram of Au/BPY/Au at different biases and indirectly deduced the I - V curve from the bias-induced shift of the single molecule peak. They showed that the I - V curve is linear around the zero bias and deflects upward around 0.3 V. The differential conductance behaves parabolically at low biases and exhibits no peaks within ± 0.7 V. However, considering the sensitivity of the electron transmission on the junction configuration mentioned above, it would be desirable to measure I - V characteristics directly on individual Au/BPY/Au junctions. In this paper, we report the results of our direct I - V measurements on Au/BPY/Au and compare the observed I - V curves with previous results and the I - V curves of Au/BDT/Au.

II. EXPERIMENTAL PROCEDURE

In order to produce Au/BPY/Au junctions, we exploited mechanically controllable break junction (MCBJ) technique, which enables us to obtain a stable single molecule junction suitable for the direct I - V measurements.²⁰ A Au wire of 0.3 mm in diameter is first fixed at two points onto a flexible substrate with an epoxy resin, and then a notch is formed on the wire at the middle of the two fixing points. Our substrate is a stainless-steel sheet of 0.2 mm in thickness, coated with a 25- μm -thick polyimide film for insulation (Ube Industries, Ltd., Upicel C). The wire/substrate assembly is mounted on a three-point bending gadget consisting of two counter supports and a pushing rod which is driven by a micrometer and

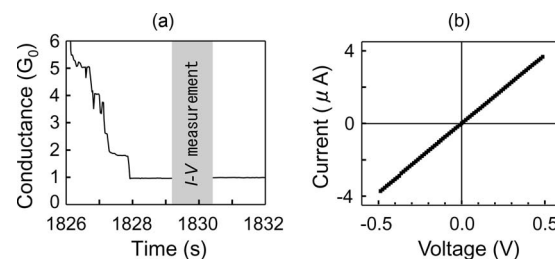


FIG. 1. (a) Typical conductance trace observed when the Au wire is broken using MCBJ. A long conductance plateau appears at $1G_0$ during which the I - V characteristics were measured in the time interval indicated by a gray strip. (b) The measured I - V curve of the $1G_0$ single-atom contact of Au.

a piezoactuator (piezosystem jena PA35/12) for coarse and fine movements, respectively. By bending the substrate with the pushing rod, the Au wire becomes stretched at the notch and makes necking deformation. Eventually, the wire breaks to form a pair of nanogapped electrodes. Before the breakage, the electrodes are connected through a couple of atoms, and the junction conductance takes some specific values. Figure 1(a) shows an example of the time evolution of the conductance in the last stage of the junction break. The conductance decreases stepwise and exhibits a plateau at $1G_0$, which is the single-atom conductance of Au. In Fig. 1(a), we stopped the substrate bending upon observing the $1G_0$ plateau, and the plateau continued over several seconds. Thus, our MCBJ has sufficient stability to hold a single-atom Au contact and measure its I - V characteristics. The I - V curve plotted in Fig. 1(b) was obtained in the time interval indicated in Fig. 1(a). Although the measurement was made in Ar atmosphere, the characteristic is completely linear up to ± 0.5 V, in good agreement with the I - V curves obtained in ultrahigh vacuum environment.^{21,22} As will be discussed later, no such linear I - V characteristics can be observed when a single molecule bridges across the Au electrodes.

For obtaining single molecule junctions, we deposited a small amount of molecular solution to the break junctions. First, we made up a BPY solution by dissolving BPY (Tokyo Kasei) into ethanol (Wako, 99.5% or 99.8% purity). Then, we prepared a Au break junction and, after breaking it to fabricate Au electrodes, placed a droplet of the BPY solution onto the break point. Because the electrode gap distance is initially larger than the BPY molecular length, BPY molecules attach to the open electrode surface but do not bridge over the gap. To prevent the adsorption saturation of BPY and leave enough uncovered electrode surface for molecular bridging,²³ the whole MCBJ assembly is quickly loaded in a vacuum chamber which is first evacuated to 1×10^{-5} Torr and then backfilled with Ar gas. Thereafter, the electrode gap is slowly narrowed to establish a single molecule junction.

We carried out two types of measurement. One is the conductance measurement where the bias voltage is fixed, and the junction is repeatedly made open and closed by increasing and decreasing the electrode gap at a constant speed of 0.03–0.06 nm/s. The transient conductance traces are measured and accumulated for statistical analyses. The other type of measurement is the I - V measurement where the junction is maintained at a specific conductance state, and a voltage ramp is applied to the junction. In either measurement, the

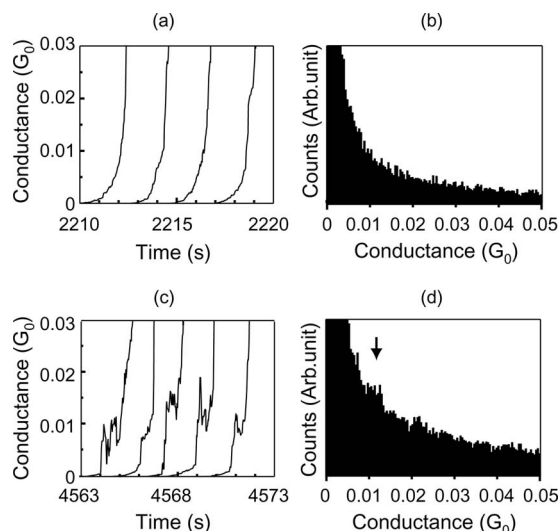


FIG. 2. [(a) and (b)] Results of the control experiment and [(c) and (d)] those of typical experiment on the Au/BPY/Au junction. Conductance traces shown in (a) and (c) were recorded during the junction closure. The resulting conductance histograms were displayed in (b) and (d). The number of traces used to construct the histogram is 362 and 343 for histograms shown in (b) and (d), respectively.

junction current is measured using a picoammeter (Keithley 6487) which also serves as a variable voltage source. The time required to obtain one I - V curve is approximately 1 s.

III. RESULTS AND DISCUSSION

A. Low bias conductance

We first measured the junction conductance of Au/BPY/Au at 0.1 V. Care was taken not to squeeze molecules in the gap, and we restricted the junction closing so that the conductance does not exceed $0.1G_0$. This upper limit is presumably higher than typical values of molecular conductance but still lower than the conductance of the smallest Au–Au contact. We can thus measure the BPY conductance without crushing the Au electrodes and destroying the BPY-adsorbed surfaces.

Figure 2 shows the results of the control experiment where only an ethanol droplet containing no BPY molecules was deposited to the junction. In this case, the conductance increases nearly exponentially with reducing the gap distance, as shown in Fig. 2(a), and exhibits no signatures of molecular bridging. As a result, the conductance histogram of the control experiment depicted in Fig. 2(b) becomes featureless. The effects of solvent molecules and other contaminations are thus negligible on the junction conductance. In contrast, when BPY molecules are present on the electrode surface, the conductance trace behaves quite differently, as shown in Fig. 2(c). Following an initial exponential increase, the conductance often exhibits a step around $0.01G_0$. Although these conductance steps are sometimes irregular, they are clearly distinguishable from noises and also from the characteristic step due to the Au–Au jump-to-contact which always occurs at $1G_0$.²⁴ Similar conductance steps have been observed in previous experiments on Au/BPY/Au (Refs. 16–19) and interpreted as indicating the formation of a single

molecule junction. We measured 343 conductance traces in total upon junction closing and constructed a histogram shown in Fig. 2(d). No data selection was made, and all traces, with or without steps, were placed into the histogram. Compared to that of the control experiment shown in Fig. 2(b), the conductance histogram reveals a peak feature around $0.01G_0$ and also a small structure around $0.02G_0$. The position of the first peak indicates that the conductance of Au/BPY/Au single molecule junction is $\sim 0.01G_0$. The structure around $0.02G_0$ would then be considered as due to the parallel bridging of two BPY molecules. Our results shown in Figs. 2(c) and 2(d) are in good agreement with previous experiments.^{16,17} In particular, the overall shape of our conductance histogram is similar to the one shown in Ref. 17. On the other hand, we found no peaks below $1 \times 10^{-3}G_0$ and could not observe the two conductance states of BPY reported by Zhou *et al.*¹⁸ and Quek *et al.*¹⁹ This does not necessarily disprove the existence of other conductance states below $1 \times 10^{-3}G_0$. Our observation of the $0.01G_0$ state of BPY suggests that this state would be more preferred in our experiment than other states of lower conductances. Quek *et al.* showed that the BPY conductance can reach $\sim 0.01G_0$ when the BPY molecule has a high tilting angle and obliquely connects the Au electrodes. If our $0.01G_0$ state really corresponds to this predicted junction configuration, such a squeezed molecular geometry would be preferred in our experiment employing MCBJ.

B. I - V characteristics

When the junction conductance shows a plateau at $0.01G_0$, we stop manipulating the electrode distance and keep it constant to hold the Au/BPY/Au junction at the $0.01G_0$ state. Typically, we can maintain the $0.01G_0$ state for several seconds. We then linearly increase the bias from 0 to ± 0.5 V and measure the I - V curve. Although we sometimes measured the I - V curve up to ± 0.8 V, most measurements were made within ± 0.5 V, where Au/BPY/Au junctions remain stable and unbroken. In the case of the Au/BDT/Au junction, the average break voltage is around 1.5 V,²⁵ and we could measure the I - V characteristics up to ± 1.0 V.²⁰ This stability difference between Au/BPY/Au and Au/BDT/Au may be explained by higher tensile strength of the Au–S bond (≥ 1.5 nN) compared to that of the Au–N bond (0.8 nN), as revealed by the break force measurements.²⁶

We obtained 70 I - V curves in total of the $0.01G_0$ state. All these curves show a linear behavior near the origin, and the zero-bias conductance is in agreement with $0.01G_0$. No I - V curves exhibit a conductance gap at the origin. At higher biases, however, the observed I - V curves exhibit a variety of nonlinear behavior which can roughly be classified into two types. One type, referred to as type-A, exhibits small nonlinearity and appears nearly straight, as shown in Fig. 3(a). On the other hand, another type, referred to as type-B and shown in Fig. 3(b), is quite nonlinear and deflects upward from the linear behavior around ± 0.3 V. As seen in the figure, type-B curve shows large diversity, and some curves are close to type-A. We found that the I - V curve often changes its type during one measurement. In one measurement, for example,

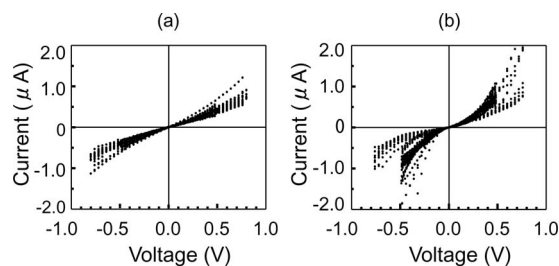


FIG. 3. Two types of the observed I - V characteristics: (a) nearly straight type-A curves and (b) nonlinear type-B curves.

we first observed type-A curves five times in sequence, and then the I - V curve switched to type-B curve, which then continued ten times. In another measurement, the I - V curve evolved as B - A - B . Considering relatively larger freedom of molecular configuration in BPY than in BDT and the sensitivity of the electron transmission to the junction geometry mentioned in Sec. I, such irreproducible changes in the I - V characteristics is not unexpected and might reflect certain changes in the junction configuration. However, the diversity in the I - V characteristics appears only at high biases, and below ± 0.3 V, both type-A and type-B curves agree with each other and yield the same zero-bias conductance of $0.01G_0$.

Figure 4(a) shows one example of relatively stable $0.01G_0$ state on which we could measure six I - V curves consecutively during the gray time intervals indicated in the figure. The results are shown in Fig. 4(b). Because this $0.01G_0$ state is formed at the first conductance jump from the break state, we can expect that this would be a fresh $0.01G_0$ state, the I - V curve of which represents the genuine transmission characteristics more properly than others produced after some junction manipulations. In fact, the observed I - V curves show fairly good reproducibility even though the plateau exhibits a conductance jump between the third and fourth measurements.

Comparison of these I - V curves with those shown in Fig. 3 reveals that five out of six I - V curves agree well with type-B curves. This result implies that type-B I - V curves might be the genuine I - V curve more likely than type-A. Also shown in Fig. 4(b) is an I - V curve obtained by Xu and Tao¹⁶ from the bias-induced shift of the single molecule peak in the

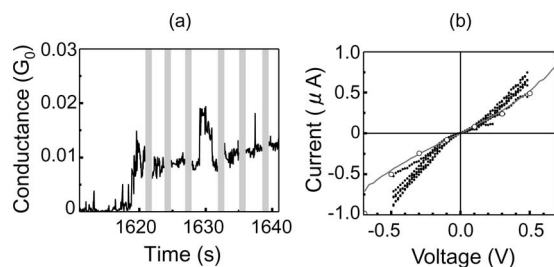


FIG. 4. (a) An example of the stable $0.01G_0$ single molecule state on which six I - V measurements were made during the time intervals indicated in the figure. (b) The measured I - V curves (black dots) are compared to the I - V curve obtained by Xu and Tao (Ref. 16) (empty circles) and a typical I - V curve of the Au/BDT/Au junction (Ref. 20) (gray line).

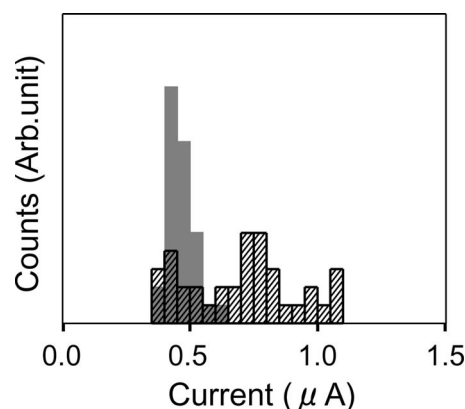


FIG. 5. Distribution of the junction current at 0.5 V. The gray and hatched histograms represent the junction current of Au/BDT/Au and Au/BPY/Au, respectively.

conductance histogram. As seen in the figure, our I - V curves tend to increase more rapidly with increasing the bias than implied by the peak-shift data. This may not be due to the difference in the experimental method because such a discrepancy between direct and indirect I - V data was not found in our previous experiment on Au/BDT/Au.²⁰ We have at this time no plausible explanation why our I - V curves differ from the one reported by Xu and Tao.¹⁶ As mentioned in Sec. I, the I - V data of Xu *et al.* are based on the conductance histogram and thus represents the statistically averaged I - V characteristics, which may not be the same as the I - V characteristics of individual junctions. Presumably, the $0.01G_0$ state shown in Fig. 4(a) may have slightly different geometries from the most typical one studied in Ref. 16.

In Fig. 4(b), we compare the six I - V curves shown in Fig. 4(b) with a typical I - V curve of the Au/BDT/Au junction at its $0.01G_0$ state.²⁰ Again, the observed I - V curves of Au/BPY/Au agree with that of Au/BDT/Au up to around ± 0.3 V but rise up more rapidly at higher biases. This means that at high biases, Au/BPY/Au can pass more current than Au/BDT/Au. To make the comparison more quantitative, we sampled the junction current at 0.5 V from the I - V curves of Au/BPY/Au and Au/BDT/Au. Sampling was made on those I - V curves where the conductance at 0.1 V before and after the I - V measurement agrees with $\pm 20\%$. The numbers of sampled I - V curves are 33 and 37 for Au/BDT/Au and Au/BPY/Au, respectively. The distribution of the current at 0.5 V is shown in Fig. 5. In the case of Au/BDT/Au, the current is narrowly distributed around $0.4 \mu\text{A}$, whereas the current of Au/BPY/Au shows a broad distribution spanning from 0.3 to $1.1 \mu\text{A}$ with a maximum around $0.8 \mu\text{A}$. Although the source of the diversity in the Au/BPY/Au junction current is left unclear, we can clearly see a difference between two distributions, i.e., at the same bias, higher junction current flows through Au/BPY/Au than Au/BDT/Au.

The I - V characteristic of a molecular junction generally reflects the electron transmission spectrum of the junction, and the position of the highest occupied molecular orbital and LUMO-originated peaks in the spectrum with respect to the Fermi level determines the current level and the shape of

the *I-V* curve. When the transmission peak resides within the half of the bias window, for example, the *I-V* curve would tend to saturate at high biases. The shape of the experimental *I-V* curves can thus provide some implications on the peak position in the electron transmission spectrum of Au/BPY/Au, and this serves to discriminate different theoretical models mentioned in Sec. I. We first point out that within the bias range of ± 0.5 V, all measured *I-V* curves exhibit positive nonlinearity and deflect upward from the linear behavior at low biases. No current saturation has been observed in our *I-V* curves. This result rules out some theoretical *I-V* curves which predict a current saturation at high biases. Also, the transmission peak of the Au/BPY/Au junction should locate at least ± 0.25 eV away from the Fermi level. On the other hand, our previous experiment showed that the *I-V* curves of Au/BDT/Au exhibit positive nonlinearity up to ± 1 V so that the transmission peak locates at least ± 0.5 eV away from the Fermi level. These observations suggest that the transmission peak of Au/BPY/Au should be closer to the Fermi level than that of Au/BDT/Au. We note that this result consistently accounts for the observed nonlinear increase in the *I-V* curve of Au/BPY/Au which occurs at lower biases than that of Au/BDT/Au.

The above result on the relative position of the transmission peak of Au/BPY/Au and Au/BDT/Au cannot, however, be directly compared to theoretical studies because many of previous transmission calculations treat either Au/BPY/Au or Au/BDT/Au but not both of them. Because the transmission features sensitively depend on theoretical details employed in each calculation, meaningful comparison cannot be made on results of different authors. Fortunately, Strange *et al.*¹⁵ recently published results of transmission calculation based on a combination of nonequilibrium Green's function theory and density functional theory, in which transmission spectra of Au/BPY/Au and Au/BDT/Au are calculated for the same atomic arrangement in the electrodes. Thus, the peak positions in two spectra can be compared to each other and with the experiment. According to their results, the distances $|E_p - E_F|$ between the lowest-lying peak and the Fermi level are ~ 0.4 and ~ 1 eV for Au/BPY/Au and Au/BDT/Au, respectively. Their spectra are thus in agreement with our result on the relative position of the transmission peak of Au/BPY/Au and Au/BDT/Au. Also, the theoretical location of the peak satisfies the conditions derived from our *I-V* experiments, i.e., $|E_p - E_F| > 0.25$ eV for Au/BPY/Au and > 0.5 eV for Au/BDT/Au. We have to note that the molecular geometry of our $0.01G_0$ may differ from the simple straight configuration assumed in Ref. 15. Despite this reservation, the agreement with theory and experiment is encouraging and will hopefully promote further investigations toward understanding the electronic structure of Au/BPY/Au.

IV. SUMMARY

Exploiting the MCBJ method, the low bias conductance and the *I-V* characteristics of Au/BPY/Au have been measured at room temperature. The conductance histogram at 0.1 V shows a peak at $\sim 0.01G_0$, in agreement with previous conductance measurements using STM. We measured the *I-V* characteristics of the $0.01G_0$ state and obtained two *I-V* curves of different nonlinearities. The results shown in Fig. 4(b) imply that type-B *I-V* curve of stronger nonlinearity might be the genuine one. All *I-V* curves show positive nonlinearity over the entire bias window ± 0.5 V and exhibit no current saturation. This indicates that the transmission peak of Au/BPY/Au locates at least ± 0.25 eV away from the Fermi level, i.e., $|E_p - E_F| > 0.25$ eV. Comparison with our previous results on Au/BDT/Au (Ref. 20) suggests that the transmission peak of Au/BPY/Au locates closer to the Fermi level than that of Au/BDT/Au, in good agreement with the latest theoretical calculations.¹⁵

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